Bottleable neutral analogues of [B2H5]- as versatile and strongly binding eta2 donor ligands

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Bottleable Neutral Analogues of $[B_2H_5]^-$ as Versatile and Strongly Binding η^2 Donor Ligands

Sunewang R. Wang, Dominic Prieschl, James D. Mattock, Merle Arrowsmith, Conor Pranckevicius, Tom E. Stennett, Rian D. Dewhurst, Alfredo Vargas,* Holger Braunschweig*

Abstract: *Herein we report the discovery that two bottleable, neutral, base-stabilized diborane(5) compounds are able to bind strongly to a number of copper(I) complexes exclusively through their B–B bond. The resulting complexes represent the first known complexes containing unsupported, neutral $\sigma_{B\text{-}B}$ diborane ligands. Single-crystal X-ray analyses of these complexes show that the X–Cu moiety (X = Cl, OTf, C_6F_5) lies opposite the bridging hydrogen of the diborane and is near perpendicular to the B–B bond, interacting almost equally with both boron atoms and causing a B–B bond elongation. DFT studies show that σ donation from and π backdonation to the pseudo-π-like B–B bond account for their formation. Astoundingly, these copper $\sigma_{B\text{-}B}$-complexes are inert to ligand exchange with pyridine under either heating or photoirradiation.*

In addition to their intriguing structural features,[1] diboranes are also powerful borylating reagents in both metal-catalyzed and metal-free methodologies for the formation of B−C bonds and other processes.[2] Generally, either oxidative addition or formal σ-bond metathesis reactions are proposed for the activation of B−B single bonds. As first proposed in the Dewar−Chatt−Duncanson model for metal-olefin complexes,[3] the synergetic combination of σ donation from a bonding ligand orbital to a vacant metal orbital and π backdonation from a filled metal orbital to the ligand antibonding orbital are the basis of the metal-promoted activation of both multiple and single bonds.[4,5] In stark contrast to the wide range of transition metal π-complexes with unsaturated molecules, only a few unsupported σ-complexes with single bonds between non-hydrogen main-group elements, such as C−C,[6] B−C[7] and Si−Si[8] bonds, have been authenticated.[4d] Despite the extensive precedent for metal-mediated activation of B−B single bonds, the synthesis of unsupported metal-diborane complexes wherein the metal binds side-on to a B−B single bond has thus far not been achieved.

In the last few decades, several interesting transition metal complexes bearing doubly base-stabilized diborane ligands bound through two metal−H−B bridges (**A**, Figure 1) have been characterized,[9-11] in addition to a number of metal complexes of anionic diborane species bound to B−B σ-bonds supported by Coulombic interactions (**B**, Figure 1).[12-15] However, unsupported transition metal complexes directly bound to the B−B single bond of neutral diboranes remain elusive. Herein we report that carbene-stabilized, hydrogen-bridged neutral diboranes(5) of the form **VII** (**C**, Figure 1), generated from an intramolecular borylborylene C−H bond insertion reaction,[16] readily coordinate to transition metals, in this case Cu(I), in an η^2 mode. This reactivity establishes neutral reagents **VII** as a highly unusual class of bottleable, neutral diboranes(5) that bind strongly to metals in a side-on, unsupported manner. These unsupported σ-complexes are surprisingly stable and inert towards ligand exchange with pyridine under either heating or photoirradiation.

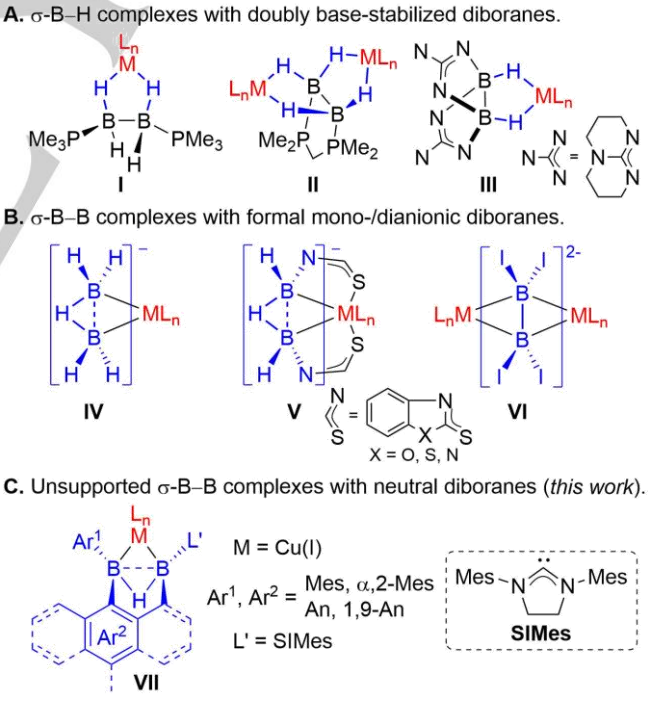

Figure 1. Coordination modes of diboranes with transition metals. Mes = 2,4,6-trimethylphenyl; α,2-Mes = methylene(3,5-dimethyl-1,2-phenylenediyl); An = 9-anthryl; 1,9-An = 1,9-anthracenediyl.

In an attempted hydride abstraction reaction of diborane **1a** with $(CuOTf)_2 \cdot$(toluene) in benzene at room temperature,[17] an intense red solution was obtained after removal of black solids by filtration, from which the unprecedented complex **2** was obtained as red crystals in 91% yield (Scheme 1).[18] Notably, complexes **3** and **4** were also obtained in good yields using less electrophilic copper(I) reagents such as CuCl and CuPf (Pf: pentafluorophenyl). Furthermore, 1,2-diboraindane **1b** also

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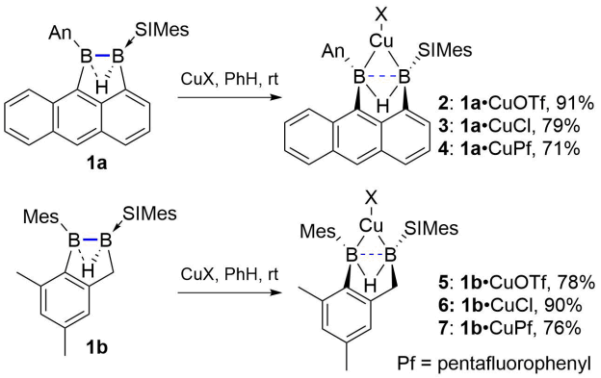
proved effective at coordinating copper(I) precursors, yielding complexes **5**−**7** in good yields. Surprisingly, the resulting CuOTf complexes **2** and **5** are inert to pyridine under either heating at 80 °C or photoirradiation, indicating that both **1a** and **1b** bind strongly as ligands.



Scheme 1. Synthesis of complexes **2**−**7**.

Molecular structures of diborane **1a** and complexes **2**−**7** derived from single-crystal X-ray crystallographic analyses are shown in Figure 2.[18] As for **1b**,[16] a hydrogen-semibridged structure was observed for **1a**. In general, complexes **2**−**7** adopt typical structures of doubly-bridged diborane(6) species,[19] with the copper units replacing one of the bridging hydrogens. The planarity of the B_2C_4 units of **1a,b** is effectively retained in complexes **2**−**7**, differing significantly from the known transition metal complexes of doubly base-stabilized diboranes(4) supported by two-fold metal−H−B interactions (**A**, Figure 1).[9-11] Notably, the elongation of the B−B distances in complexes **2**−**7** (1.762(2)−1.795(3) Å) with respect to the unbound diborane ligands (**1a**: 1.682(3) Å; **1b**: 1.670(3) Å)[16] is more pronounced than observed upon metal coordination of base-stabilized diborenes (LRB=BRL), indicating a larger degree of covalent character in complexes **2**−**7**. Moreover, this elongation also distinguishes the title compounds from the only reported mononuclear complex of a base-free diborene (RB=BR), which shows "bond-strengthening" π backbonding.[5] Longer B−B and shorter B−Cu distances, indicative of stronger metal-diboron orbital interactions, were observed with the more electrophilic copper centers. Thus, the B−Cu distances in CuOTf complexes **2** (2.068(2), 2.087(2) Å) and **5** (2.072(2), 2.079(2) Å) are significantly shorter than those of the diborene (B=B) copper complexes (averaging 2.138 and 2.148 Å),[17,20] and are comparable to diboryne (B≡B) copper complexes (averaging 2.077-2.089 Å)[21] and even a tetranuclear copper(I) boryl complex (averaging 2.083 Å), which was shown to react with an enone as a boron nucleophile.[22]

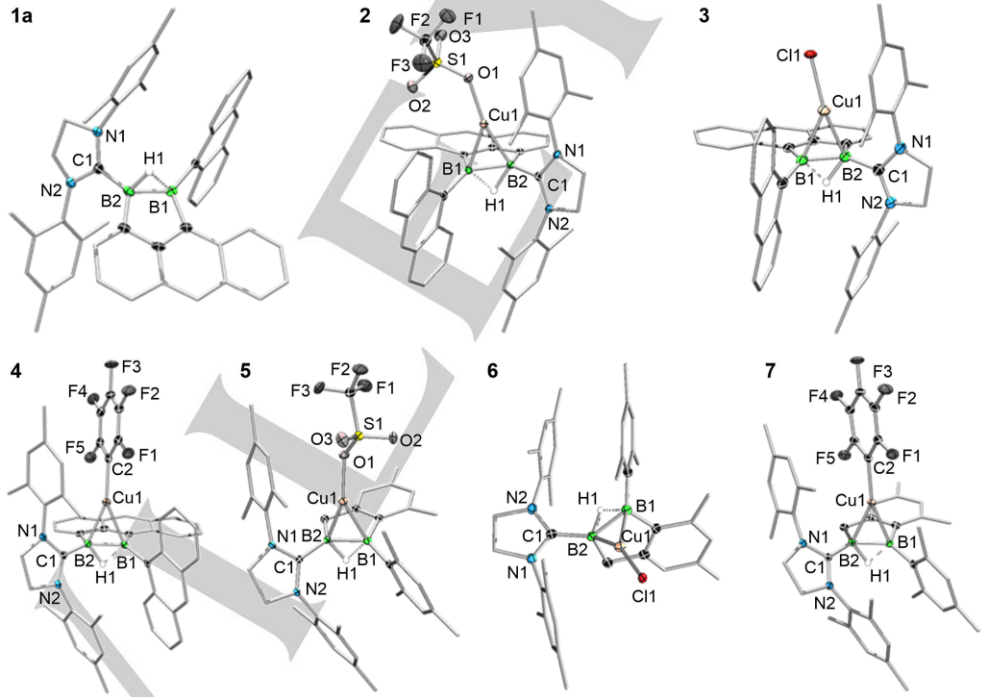


Figure 2. Molecular structures of compounds **1a** and **2**−**7**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms except the bridging hydrogen atoms, solvent molecules and one molecule of **1a** and **6** in the unit cell have been omitted for clarity. Selected bond lengths [Å] and angles [°] for **1a**: B1−B2 1.682(3); B1−H1 1.49(2); B2−H1 1.20(2); $\Sigma\angle_{B1}$ 359.8; $\Sigma\angle_{B2}$ 358.5. **2**: B1−B2 1.795(3); B1−Cu1 2.087(2); B2−Cu1 2.068(2); B1−H1 1.35(2); B2−H1 1.26(2); Cu1−O1 1.920(1); $\Sigma\angle_{B1}$ 355.9; $\Sigma\angle_{B2}$ 358.7. **3**: B1−B2 1.778(6); B1−Cu1 2.107(3); B2−Cu1 2.074(4); B1−H1 1.32(4); B2−H1 1.23(5); Cu1−Cl1 2.1731(9); $\Sigma\angle_{B1}$ 356.3; $\Sigma\angle_{B2}$ 358.7. **4**: B1−B2 1.769(3); B1−Cu1 2.139(2); B2−Cu1 2.085(2); B1−H1 1.36(2); B2−H1 1.19(2); Cu1−C2 1.938(2); $\Sigma\angle_{B1}$ 356.7; $\Sigma\angle_{B2}$ 358.7. **5**: B1−B2 1.779(3); B1−Cu1 2.079(3); B2−Cu1 2.072(2); B1−H1 1.36(2); B2−H1 1.19(2); Cu1−O1 1.908(1); $\Sigma\angle_{B1}$ 357.5; $\Sigma\angle_{B2}$ 359.1. **6**: B1−B2 1.767(5); B1−Cu1 2.090(4); B2−Cu1 2.067(3); B1−H1 1.35(5); B2−H1 1.26(4); Cu1−Cl1 2.150(1); $\Sigma\angle_{B1}$ 357.1; $\Sigma\angle_{B2}$ 358.3. **7**: B1−B2 1.762(2); B1−Cu1 2.117(2); B2−Cu1 2.107(2); B1−H1 1.37(2); B2−H1 1.21(2); Cu1−C2 1.939(2); $\Sigma\angle_{B1}$ 357.6; $\Sigma\angle_{B2}$ 359.4.

Formally, protonation of the diboranyl anion $B_2H_5^-$ would give diborane(6) (B_2H_6), resulting in B−B single bond cleavage.[23] In accordance with the isolobal analogy between diboranes **1a**,**b** and $B_2H_5^-$, coordination of diboranes **1a**,**b** and $B_2H_5^-$ to transition metals with weak π-backdonating ability should similarly lead to activation of the B−B single bonds. Indeed, the B−B distances in complexes **2**−**7** are comparable to those in complexes **IV** (**B**, Figure 1) (Mo: 1.796(6) Å; Fe: 1.773(8) Å)[12] and complex **V** with two additional chelating bonds (Ru: 1.776(4) Å),[14] which are within the range of the B−B distances in hydroborane dimers.[19] On the other hand, the B−B distance in a diplatinum(II) complex of $[B_2I_4]^{2-}$ (1.744(9) Å) is slightly shorter (**VI**, Figure 1), which was ascribed to the stronger π backdonation from the Pt(II) centers to the diboron fragments, as confirmed by DFT studies.[15]

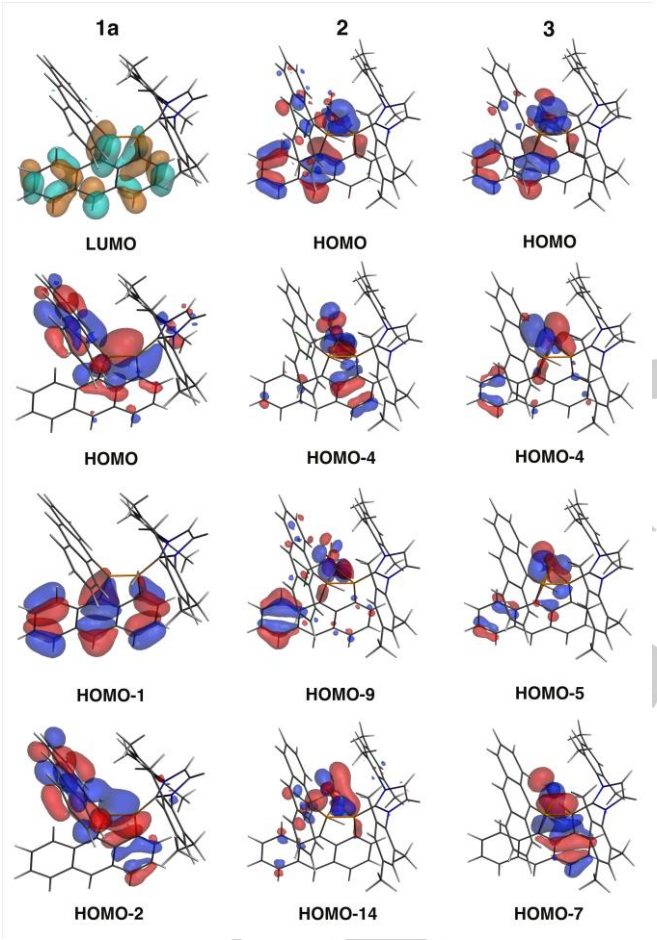


Figure 3. Selected frontier molecular orbitals of **1a**, **2** and **3**.

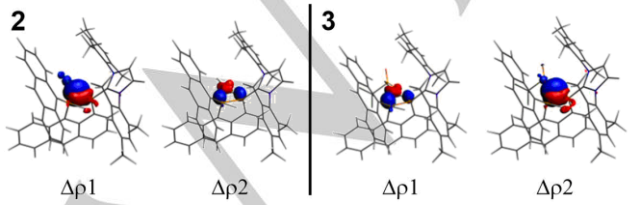


Figure 4. Charge deformation densities of **2** and **3**. Charge flow from red to blue.

Kohn-Sham DFT studies on diborane **1a** and complexes **2** and **3** in the gas phase were then carried out to elucidate their electronic structures. Interestingly, two of the occupied MOs of **1a** (HOMO and HOMO-2) show significant lobes of π symmetry at the B−B bond, while the LUMO and HOMO-1 show BB π* character conjugated with the anthryl π orbitals (Figure 3). Although both HOMOs of **2** and **3** show no obvious interactions between B_2 and copper, inspection of the intrinsically located frontier orbitals of **2** and **3** related to the Cu−B_2 interactions indicates the familiar Dewar-Chatt-Duncanson σ donation (HOMO-4, HOMO-14 for **2** and HOMO-5, HOMO-7 for **3**) and π backbonding (HOMO-9 for **2** and HOMO-4 for **3**) in the current neutral diborane-copper complexes (Figure 3),[12b] which is consistent with the first and second charge deformation density plots of **2** and **3** (Figure 4). Furthermore, the electron localization maps along the MB_2 plane (Figure 5) for **2** and **3** confirm polarization of the B−B charge density towards the copper center, indicating stronger σ donation than π backdonation in these complexes. Energy decomposition analysis on **2** and **3** indicates both stronger orbital and electrostatic interactions in **2** than those in **3**, with the orbital interaction being more strengthened (8.8% vs 5.7%). The Pauli repulsion, however, changes very little (Table 1), which is in accordance with the aforementioned longer B−B and shorter B−Cu distances observed with the more electrophilic copper species.

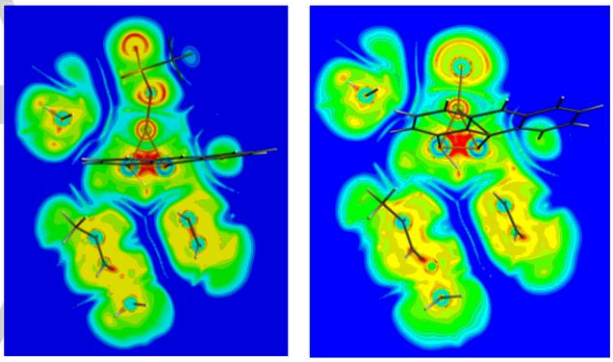


Figure 5. Electron localization maps of **2** and **3** in the Cu−B_2 plane derived from SEDD calculations. Red indicates high electron density, blue indicates low electron density.

Table 1. Energy Decomposition (in kcal mol^{-1}) for 2 and 3 Calculated via ETS-NOCV at the OLYP/TZ2P Level

	E_{Pauli}	E_{OrbInt}	E_{Elsta}	E_{int}
2	142.74	−70.16	−132.03	−59.45
3	145.62	−64.47	−124.95	−43.80

Closer investigation of the changes in Hirshfeld charge upon complexation shows that the (non-NHC-bound) B1 atom significantly gains negative charge (+0.033 to –0.002 in **2** and –0.005 in **3**) while the (NHC-bound) B2 (–0.071 to –0.062 in **2** and –0.065 in **3**), NHC carbon atom (+0.077 to +0.082 in **2** and **3**), and bridging hydrogen (–0.011 to +0.003 in **2** and +0.001 in **3**) all slightly lose negative charge. This is consistent with the shortening of the B1-H bond upon complexation observed crystallographically. Accordingly, the Mayer bond orders of the B2-H bonds decrease (0.58 to 0.51 in **2** and **3**) while those of the B1-H bonds increase (0.32 to 0.39 in **2** and 0.38 in **3**) significantly upon complexation. This is accompanied by a very large decrease in B−B bond order (0.85 to 0.41 in **2** and 0.43 in

3), as would be expected from the donation of electron density from the B-B bond to the Cu center.

In solution, the complexation of copper to the diboranes **1a**,**b** causes significant ^{11}B NMR (CD_2Cl_2) upfield shifts for the non-NHC-bearing boron centers (**1a**: δ 55.8; **1b**: δ 53.1; **2**−**7**: 27.9−30.1 ppm), while resonances of the NHC-bearing boron atoms are moved slightly downfield (**1a**: δ 2.6; **1b**: δ 1.5; **2**−**7**: 3.1−6.2 ppm). In ^{11}B-decoupled ^{1}H NMR spectra (CD_2Cl_2), the resonances for the boron-bound hydrogen atoms shift 0.4−0.9 ppm upfield upon coordination to copper(I).[18] The $^{1}J_{B,H}$ coupling constant in **2** was determined to be 145 Hz by the analysis of the cross-peak profile in its ^{11}B-^{1}H HMQC NMR spectrum, similar to previously reported compounds with unsymmetrical B−H−B bridges in the solid state.[16,24]

The infrared spectra of **2** both in solution and the solid state are free of bands attributable to terminal B−H vibrations. Distinct bands are observed at 1606 and 1607 cm^{-1} in solid and solution IR spectra, respectively, matching those attributed by Himmel et al. for similarly unsymmetrically-bridging hydride stretches in triborane compounds (1610 and 1614 cm^{-1}).[24] However, this stretch is computationally predicted to appear at ca. 2037 cm^{-1} in **2**, making the stretching band at ca. 1610 cm^{-1} unlikely to be that of the bridging B-H.

The UV-vis absorption spectrum of free ligand **1a** shows a very weak shoulder at around 470 nm, most likely the forbidden intraligand charge transfer (HOMO to LUMO transition, Figure 3). The longest wavelength shoulder bands of Cu complexes **2** and **3**, both slightly below 500 nm, are both stronger than that of **1a**, making these bands likely the mixed [π-π* + MLCT] transitions (HOMO to LUMO, Figure 3).

In conclusion, unsupported $\sigma_{B\text{-}B}$-complexes of copper with carbene-stabilized neutral diboranes were synthesized for the first time in good to excellent yields. Crystallographic analysis confirmed that this novel side-on coordination mode, which lacks the conventional metal−H−B bridges of other complexes, effectively activates the B−B single bond, which may shed some light on the understanding of transition metal-catalyzed borylation reactions with diboron compounds.[2] The exceptional ligating properties of neutral diboranes(5) like **1a** and **1b** may open new possibilities for the development of robust metal complexes containing strongly-binding, neutral ligands bound through their B−B bonds.

Acknowledgements

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Keywords: σ-complexes; diboranes; copper; boron; density functional theory

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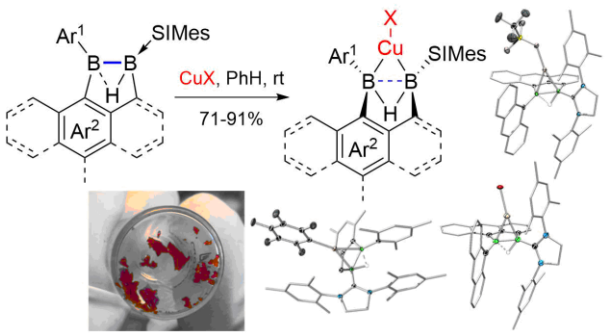

Herein we report the discovery that two bottleable, neutral, base-stabilized diborane(5) compounds are able to bind strongly to a number of copper(I) complexes exclusively through their B-B bond. The resulting complexes represent the first known complexes containing unsupported, neutral $\sigma_{B\text{-}B}$ diborane ligands.

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